

Slater-Pauling behavior in half-metallic magnets

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We review the appearance of Slater-Pauling rules in half-metallic magnets. These rules have been derived using ab-initio electronic structure calculations and directly connect the electronic properties (existence of minority-spin energy gap) to the magnetic properties (total spin magnetic moment) in these compounds. Their exact formulation depends on the half-metallic family under study and they can be easily derived if the hybridization of the orbitals at various sites is taken into account.

Keywords: Electronic Structure Calculations, Magnetism, Half-metals, Slater-Pauling

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INTRODUCTION

The developments in electronics, combining the magnetic and semiconducting materials (so-called magnetoelectronics or spintronics) [1–3], have brought half-metallic magnets, initially predicted by de Groot and collaborators in 1983 [4], to the center of scientific research. In these materials the two spin bands show a completely different behavior. While the spin-up electronic band structure is metallic, in the spin-down band the Fermi level falls within an energy gap as in semiconductors [5]. Such half-metallic compounds exhibit, ideally, a 100% spin polarization at the Fermi level and therefore they should have a fully spin-polarized current and be ideal spin injectors into a semiconductor, thus maximizing the efficiency of spintronic devices [6].

The interest on half-metallic magnets has been mainly focused on the Heusler compounds. There are two distinct families of Heuslers. The so-called full-Heuslers, with the chemical formula X_2YZ , crystallize in the $L2_1$ structure which consists of four fcc sublattices, where X is a high valent transition or noble metal atom, Y is a low-valent transition metal atom and Z is a sp element [7, 8]. In Fig. 1 we present the lattice structures of all the compounds revised in this Short Review. The second class of Heuslers encompass the so-called semi- (or half-) Heusler compounds of the chemical form XYZ , crystallizing in the $C1_b$ structure. The structure as shown in Fig. 1 is similar to the $L2_1$ one but now one of the four sites along the diagonal is empty. NiMnSb, a semi-Heusler, was the first one predicted to be a half-metal in 1983 by de Groot and collaborators [4]. The main advantages of Heusler alloys with respect to other half-metallic systems (e.g. some oxides like CrO_2 and Fe_3O_4 and some manganites like $La_{0.7}Sr_{0.3}MnO_3$) [9] are their relatively high Curie temperatures T_C [7, 8] (while for the other compounds T_C is near the room temperature, e.g. for NiMnSb it is 730 K

and for Co_2MnSi it reaches the 985 K [7]) as well as their structural similarity to the zincblende structure, adopted by binary semiconductors widely used in industry (such as GaAs on ZnS).

In 2000, Akinaga and collaborators [10] reported growth of a few layers of CrAs in the metastable zincblende phase (zb) for the first time; this was achieved by molecular beam epitaxy on a GaAs substrate (the ground state structure of CrAs is the MnP structure). In the zb phase, CrAs was reported to be ferromagnetic, with a Curie point higher than 400 K. In the same publication, first-principles calculations of bulk zinc-blende CrAs showed the material to be a half-metallic ferromagnet; the moment per formula unit was calculated to be $3 \mu_B$, in agreement with the experimental result. These findings initiated a strong activity on the transition metal (TM) pnictides and chalcogenides, because several merits were combined as in Heusler compounds mentioned above: the half-metallic property, coherent growth on a semiconductor, and T_C higher than room temperature. The activity was extended beyond zb CrAs, encompassing a variety of tetrahedrally bonded TM compounds with sp atoms of the IV, V and VI groups of the periodic table [11].

Except the TM pnictides and chalcogenides, the half-metallic property was also predicted in another class of binary materials the so-called sp-electron ferromagnets or d⁰-ferromagnets [12]. In two pioneering papers published by Geshi et al [13] and Kusakabe et al [14], it was shown using first-principles calculations that CaP, CaAs and CaSb compounds present half-metallic ferromagnetism when grown in the zincblende structure. Several first-principles calculations have been carried in several I/II-IV/V compounds and it was shown that they are half-metallic magnets in all three zincblende, wurtzite and rocksalt (rs) metastable structures; the ground state in all cases being the rs lattice [15–17]. In Fig. 1 we

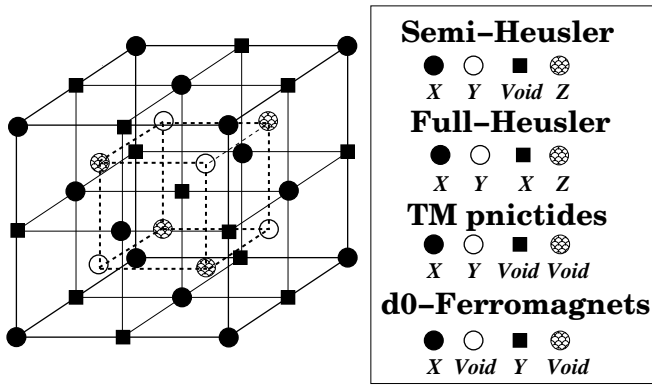


FIG. 1: Schematic representation of (i) the $C1_b$ cubic structure adopted by the semi-Heusler compounds, (ii) the $L2_1$ structure adopted by the full-Heusler compounds, (iii) the zinc-blende structure adopted by the transition-metal pnictides and chalcogenides, and (iv) the rocksalt structure of the d^0 -ferromagnets. The cube contains exactly four unit cells.

present both the zb and rs structures which are similar to the cubic lattice of the Heusler compounds with two voids per unit cell. Evidence of the growth of such nanostructures has been provided by Liu et al who have reported successful self-assembly growth of ultrathin CaN in the rocksalt structure on top of Cu(001) [18]. Finally we have to note that materials containing C or N seem to be more promising for applications since the Hund energy for the light atoms in the second row of the periodic table is similar to the Hund energy of the 3d transition metal atoms.

Slater and Pauling had shown in two pioneering papers that in the case of binary magnetic compounds when we add one valence electron in the compound this occupies spin-down states only and the total spin magnetic moment decreases by about $1 \mu_B$ [19, 20]. Interestingly a similar behavior can be also found in half-metallic magnets as confirmed by first-principles (ab-initio) electronic structure calculations. In the half-metallic alloys the spin-down band-structure is fixed; the number of spin-down occupied bands and their character does not change among the half-metallic members of the same family of compounds. The extra valence electron now occupies exclusively spin-up states increasing the total spin magnetic moment by about $1 \mu_B$. It was shown that in the case of the semi-Heusler compounds like NiMnSb the total spin magnetic in the unit cell, M_t scales, as a function of the total number of valence electrons, Z_t , following the relation $M_t = Z_t - 18$ [21], while in the case of the $L2_1$ full-Heuslers this relation becomes $M_t = Z_t - 24$ [22]. Moreover for the TM pnictides and chalcogenides as well as the d^0 -ferromagnets the corresponding rule takes the form $M_t = Z_t - 8$ although its origin is different in the two families of compounds [15, 16, 23]. These Slater-Pauling (SP) rules connect the electronic properties (appearance

of the half-metallic behavior) directly to the magnetic properties (total spin magnetic moments) and thus offer a powerful tool to the study of half-metallic compounds since (i) magnetic measurements can be used to confirm the half-metallic character of a compound, and (ii) simple valence electrons counting can predefine the magnetic properties of a half-metal. The aim of the present Short Review is to provide an overview of the origin of the SP rule in all mentioned families of half-metallic magnets as derived from electronic structure calculations based on the density functional theory.

HEUSLER COMPOUNDS

The most studied half-metallic magnets are the Heusler compounds. We will start our discussion from the case of semi-Heuslers, like NiMnSb, since it was the first to be predicted to be a half-metal [4]. The role of the sp element is to provide in the spin-down electronic band structure a single s and a triple-degenerated p band deep in energy; they are located below the d -states and accommodate d -charge from the transition metal atoms. In Fig. 2 we present schematically the character of the bands and their degeneracy in the spin-down band structure. The bands below the Fermi level are occupied while the ones above it are empty. The d -orbitals of the two transition metal atoms hybridize strongly creating five occupied bonding and five unoccupied antibonding d -states in the spin-down band structure [21]. Each set of five occupied(unoccupied) d -hybrids contains the double degenerated e_g and the triple degenerated t_{2g} states. Note that the notations e_g and t_{2g} are, strictly speaking, valid only for states at the center of the Brillouin zone; however, the energy bands formed by them are energetically rather separated, and therefore this notation can be used to describe the different bands. As a result there are in total exactly nine occupied spin-down states and the SP relation is $M_t = Z_t - 18$, where M_t is the total spin magnetic moment in μ_B and Z_t the total number of valence electrons [21]. The number of the occupied spin-down states is always kept equal to nine for all half-metallic semi-Heusler compounds (the Fermi level is fixed within the spin-down energy gap) and does not depend on the chemical species of the constituent atoms and thus the total spin magnetic moment depends only on the number of valence electrons and not on the specific chemical type of the half-metal, *e.g.* FeMnSb and CoCrSb have both 20 valence electrons and a total spin magnetic moment of $2 \mu_B$. When the total spin magnetic moment is positive and thus are more than 18 valence electrons in the unit cell, in the spin-up band structure all nine bonding s -, p - and d -states are occupied, as in the spin-down band, and the extra charge occupies the antibonding spin-up states [21]. In Fig. 3 we have gathered the calculated total spin magnetic moments versus the total number of

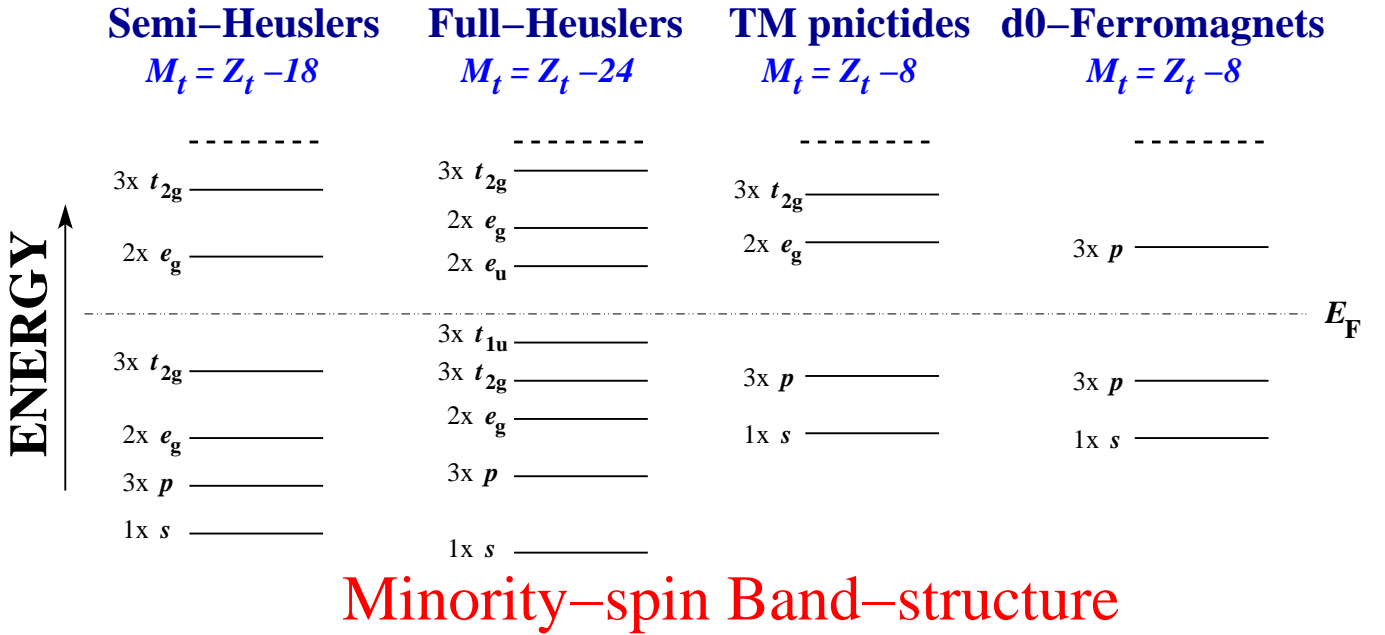


FIG. 2: Schematic representation of the energy levels of the minority-spin electronic band structure for all four families of half-metallic magnets under study. Below the Fermi level are located the occupied states. Numbers in front of orbitals denote the corresponding degeneracy. For the definition of the orbitals see text.

valence electrons for some selected representative semi Heusler compounds. A special case is MnCrSb, which has a zero total spin magnetic moment but Mn and Cr atoms possess large antiparallel spin magnetic moments [24]. These compounds are known as half-metallic antiferromagnets and are of technological importance since they create in-principle zero external fields and thus minimal energy losses in devices.

In the case of the half-metallic L2₁ full-Heuslers the origin of the SP rule is more complicated due to the more complicated hybridization effects between the d -orbitals [22]. The sp element provides in the spin-down electronic band structure a single s and a triple-degenerated p band deep in energy as for the semi-Heusler compounds. With respect to the d -orbitals, one has first to consider the interaction between the X elements. Although the symmetry of the L2₁ lattice is the tetrahedral one, the X elements themselves, if we neglect the Y and Z atoms, form a simple cubic lattice and sit at sites of octahedral symmetry [22]. The d -orbitals of the neighboring X atoms hybridize creating five bonding d -states, which after hybridize with the d -orbitals of the Y atoms creating five occupied and five unoccupied d -hybrids, and five non-bonding d -hybrids of octahedral symmetry (the triple-degenerated t_{1u} and double-degenerated e_u states). These non-bonding hybrids cannot couple with the orbitals of the neighboring atoms, since they do not obey the tetrahedral symmetry, and only the t_{1u} are occupied leading to a total of 12 occupied spin-down states and

the SP relation is now $M_t = Z_t - 24$ [22]. In the case of full-Heusler compounds when $Z_t > 24$ the spin-up non-bonding e_u states are the first to be occupied followed by the antibonding states, while when $Z_t < 24$ the Fermi level crosses either the spin-up non-bonding t_{1u} states or the spin-up bonding d -states [22]. In Fig. 3 we have gathered some representative cases of calculated half-metallic full-Heusler compounds. The total spin magnetic moment can be: (i) zero as for Cr₃Se, which is a half-metallic antiferromagnet [25], (ii) positive when $Z_t > 24$ going up to a maximum value of 5 μ_B for Co₂MnSi (it has been reported that electronic correlation restores half-metallicity in Co₂FeSi which has a total spin magnetic moment of 6 μ_B [26]), or (iii) negative as for the half-metallic ferromagnetic Mn₂VGe and Mn₂VAI compounds where the V spin moment is antiparallel to the spin moment of the Mn atoms [27].

BINARY COMPOUNDS

TM pnictides & chalcogenides

The principal mechanism leading to the appearance of the half-metallic gap in zincblende compounds of transition metals (TM) with sp elements is the hybridization of the d wavefunctions of the TM atom with the p wavefunctions of the sp atom [23]. This p - d hybridization is dictated by the tetrahedral environment, where each atom is

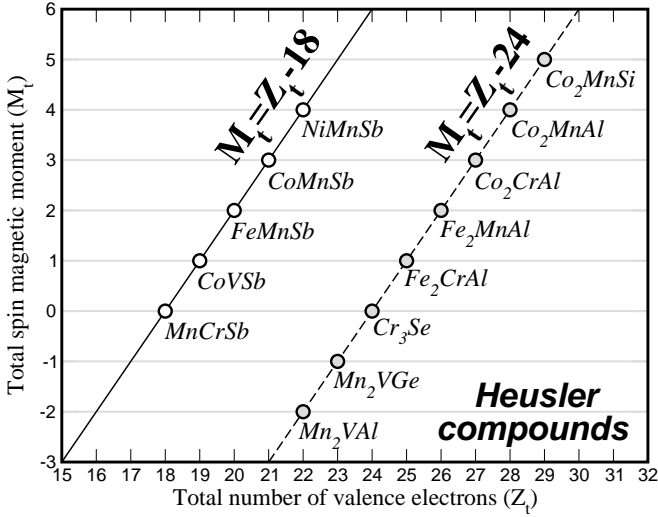


FIG. 3: Calculated total spin magnetic moments, M_t , in μ_B as a function of the total number of valence electrons, Z_t , in the unit cell for selected representative semi- and full-Heusler compounds. The two lines represent the two variants of the Slater-Pauling rule followed by the two families of Heuslers.

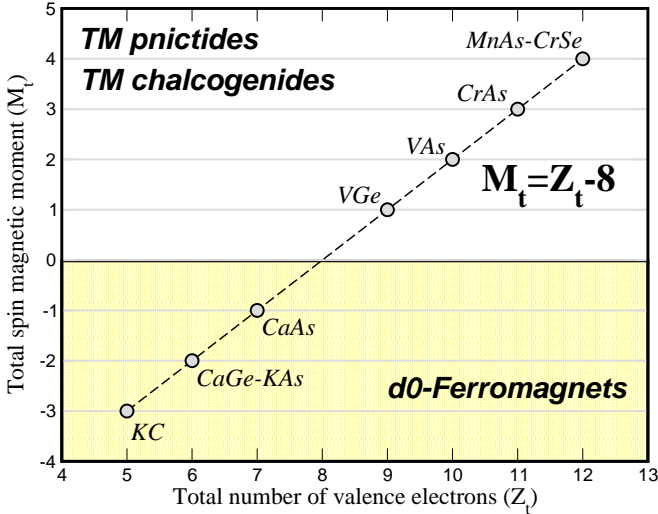


FIG. 4: Similar to Fig. 3 for the binary half-metallic magnets under study. Both transition-metal pnictides (chalcogenides) and d⁰-ferromagnets follow the same Slater-Pauling rule despite the different origin of the rule (see Fig. 2).

surrounded by four atoms of the other species as shown in Fig. 1. In particular, in the presence of tetrahedral symmetry the d -states split in two irreducible subspaces: the t_{2g} threefold-degenerate subspace, consisting of the d_{xy} , d_{yz} and d_{zx} states, and the twofold-degenerate e_g subspace, which includes the $d_{x^2-y^2}$ and d_{z^2} states. Only

states of the former subspace can hybridize with the p states of the sp -atom neighbors, forming bonding and antibonding hybrids. In the spin-down band structure the bonding states are mainly of p character while the antibonding states of t_{2g} character. The e_g states of the TM atom, on the contrary, remain rather non-bonding. The situation is shown schematically in Fig. 2 for the spin-down band structure. Below the Fermi level there is a single-degenerated s -band due to the sp atom followed by the bonding $p-d$ hybrids which are mainly of p character with a small t_{2g} admixture. Above the Fermi level are the non-bonding TM e_g states followed by the antibonding $p-d$ hybrids which are mainly of t_{2g} character.

Thus for the transition-metal pnictides and chalcogenides there are in total four occupied states in the spin-down band-structure and the SP rule becomes $M_t = Z_t - 8$ [23]. In Fig. 4 we have gathered the calculated total spin magnetic moment for some transition metal pnictides and chalcogenides versus the total number of valence electrons. The total spin magnetic moment can vary from 1 μ_B for VGe which has 9 valence electrons per unit cell up to 4 μ_B for MnAs and CrSe which have 12 valence electrons. Compounds with 13 valence electrons like MnSe prefer to be antiferromagnets that half-metallic ferromagnets since in the latter case all antibonding $p-d$ hybrids in the spin-up band-structure should be occupied which is energetically unfavorable [23].

d⁰-Ferromagnets

In the case of d⁰-ferromagnets like CaAs the SP rule is identical to the TM pnictides and chalcogenides if we consider that the energy gap is located in the spin-down band structure; in most references like [15–17] the energy gap is considered to be located in the spin-up band structure and the SP rule is $M_t = 8 - Z_t$. Its origin is different than the TM pnictides, discussed above since the d⁰-ferromagnets are made up of two sp atoms and thus no $p-d$ hybridization is present. In the spin-down band-structure the s and p orbitals of the two sp atoms hybridize creating bonding and antibonding hybrids. In the spin-down band-structure, as shown in Fig. 2, the bonding s and p states are occupied while the antibonding ones are empty leading to a total of 4 occupied spin-down bands. In the spin-up band structure the bonding s state is occupied and the Fermi level crosses the bonding p -states since we have less than 8 valence electrons in the unit cell (compounds with 8 valence electrons like CaS are semiconductors). In Fig. 4 we have gathered the calculated total spin magnetic moments for some representative d⁰-ferromagnets and the total moment ranges from -3 μ_B for KC which has just 5 valence electrons per unit cell up to -1 μ_B for CaAs which has 7 valence electrons in the unit cell. Finally we should note that the arguments

just presented are valid for both the rocksalt (which is the most stable structure) and the zincblende structure since as presented in Fig. 1 both obey the tetrahedral symmetry and similar symmetry arguments are valid.

CONCLUSIONS

Half-metallic magnets are a special class of materials which has attracted considerable attention in spintronics/magnetoelectronics due the predicted perfect spin-polarization of the electrons at the Fermi level. In the case of Heusler and binary half-metallic compounds, it is possible to formulate Slater-Pauling rules which connect directly the electronic properties (number of valence electrons in the unit cell) to the magnetic properties (total spin magnetic moment in the unit cell). The Fermi level is fixed within the spin-down energy gap and extra electrons accommodate exclusively spin-up states. These rules are a strong tool in the study of the half-metallic magnets since: (i) magnetic measurements can be employed to confirm the half-metallic character of samples, and (ii) the chemical formula of a half-metallic compound predefines its total spin magnetic moment. The origin of the Slater-Pauling rule differs in the various families of compounds under study and for each case the possible hybridization of the orbitals with respect to both the local and the crystal's symmetry should be taken into account. In semi-Heusler compounds, like NiMnSb, the hybridization of the d -orbitals leads to a $M_t = Z_t - 18$ relation, where M_t the total spin magnetic moment in μ_B and Z_t the total number of valence electrons in the unit cell. In the case of full-Heuslers, like Co₂MnSi, the existence of d -hybrids of octahedral symmetry located exclusively at the Co sites leads to a more complicated hybridization effect and a $M_t = Z_t - 24$ rule. Finally for both type of binary compounds the Slater-Pauling rule is $M_t = Z_t - 8$ but its origin is the $p-d$ hybridization in the transition-metal pnictides and chalcogenides and the $p-p$ hybridization in the d^0 -ferromagnets.

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